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Short Communication

Electroluminescence and the measurement of temperature during Stage III of flash sintering experiments

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Abstract

The optical glow of ceramics that becomes established during the constant state of flash, known as Stage III in flash sintering experiments, is investigated. The specimen temperature in this state is obtained from in situ experiments at the Pohang Light Source II. The measurements of the specimen temperature agree very well with the predictions from the black body radiation model. The optical emission spectrum from the specimen is measured from the visible into the deep infrared, and compared with black body radiation that would have been expected from Joule heating. It is concluded that the specimens radiate by electroluminescence, which is ascribed to electron–hole recombination of excitons. The phenomenon is likely the same as discovered by Nernst at the turn of the twentieth century.

Keywords: Flash sintering; Electroluminescence; Joule heating; Stage III

1. Introduction

The first experiment of flash sintering was carried out by applying an electric field to a dog-bone shaped "green" specimen with a pair of platinum wires, which also served the purpose of suspending the specimen into a furnace [1]. The furnace was heated at a constant rate until the specimen flashed and sintered in just a few seconds. Sintering was accompanied by an abrupt rise in the conductivity of the specimen, which was stabilized by switching to current control [2]. The sample then reached a dynamic equilibrium between its temperature and its conductivity driven by I^2R heating, the product of the second power of the current and the resistance of the specimen. The rise in temperature would lower the resistance of the specimen. As a result the power expended in the specimen would decline and the specimen would tend to cool. Cooling would raise the resistance and power would rise. In this way a dynamic equilibrium where the power dissipation remains at a constant value is established. We called this Stage III of the flash sintering experiment [2]. Note that the specimen sinters during the transient prior to reaching Stage III. Therefore the constant state of flash pertains to dense samples.

In recent work, we have conducted flash experiments with pre-sintered specimens that are prepared either in situ, that is sintered under the electric field, or separately by conventional sintering. These dense samples flash in the same way as the green samples, exhibiting the three stages, incubation, transient and eventually steady state under current control. The present work is an exposition of the behavior of the dense samples, made from 3YSZ (3 mol% yttria stabilized zirconia), in Stage III where they stay in a steady state.

The experiments reported here pertain to the measurement of the specimen temperature from lattice expansion during in situ experiments at the Pohang Light Source (PLS II). We discover the temperatures to be modest which does not explain why the specimens glow intensely when they are in this state. We present

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measurements of the luminescence spectra and compare it to the spectra that would have been expected should the specimen have radiated as a black body. We conclude that the specimens exhibit luminescence that is characteristic of electron–hole recombination of excitons.

The first report on optical emission was published in 2014 [3] where it was shown that the intensity of emission was coupled to the electrical conductivity of the specimen. These results are have been reproduced by Muccillo and Muccillo [4].

2. Experimental materials and methods

The specimens for the in situ experiments at PLS II were prepared from 3YSZ powders (TZ-3YB, Tosoh USA, Grove City, OH) with a particle size of 60 nm. The samples had a gage length of 3.25 mm and a rectangular cross section of 1.30 mm × 0.58 mm. The volume to surface ratio of the specimens was equal to 0.20 mm. The handles of the dog bones were attached to an alumina sample holder tube by the means of two platinum wires, which also carried electricity to the specimen. Platinum paste was used to ensure good electrical contact. A thin and shallow channel, approximately 200 μm wide and 50 μm deep, oriented normal to the current path, was cut into one side of the specimen. It was filled with platinum paste, which was used as a reference for measuring the specimen temperature. However, this small amount of platinum would evaporate at temperatures above about 1350 °C, thus limiting its use as a standard only up to this temperature. We also measured the lattice expansion of 3YSZ, which was matched to the platinum reference, but could then be extended up to the highest temperature of the furnace, which was near 1600 °C. In this way a calibration curve for lattice expansion versus specimen temperature, ranging from 800 °C up to 1690 °C could be obtained.

The in situ X-ray diffraction experiments were carried out on the beam line 5A Material Science XRS at the PLS II. The light source provided hard X-rays from an in-vacuum undulator and had a wavelength of 0.69265 Å or 17.9 keV. The focused beam size had a width of 600 μm and a height of 400 μm. A point scintillator detector Cyberstar X2000 (Oxford Danfysik) was used to detect the scattered X-rays. Since the sample width was larger than the beam spot, the center position was found by sweeping the beam spot across the sample at a fixed scattering angle. The beam spot position was chosen where the intensity was at a maximum. While this method yielded self-consistent results for one sample configuration, it would have caused a slight difference in absolute peak position from sample to sample, with a deviation of $2\theta = \pm 0.003^\circ$, which led to an uncertainty ±15 °C in the estimate of the specimen temperature. The lattice expansion was measured from the shift in the diffraction peaks relative to the peak for 800 °C. The X-ray diffraction peaks were acquired at approximately one-minute intervals.

The configuration of the furnace and the sample holder for the experiments at PLS II are shown in Fig. 1. A special furnace was built with narrow slits cut in for the ingress and the exit of the diffracted X-ray beams, over the angular range of −10° to 60°. The platinum wire heating element enabled a maximum furnace temperature of 1690 °C. The inside diameter of the hot zone was 4 mm, just large enough to accommodate the specimen holder, while the length of the hot zone was four times the length of the specimen; in this way the temperature along the hot zone was kept within ±3 °C.

All flash experiments were carried out at a constant furnace temperature of 800 °C. The electric field was applied to the sample from a 600 W DC power supply (Sorensen 300-2, Sorensen, San Diego, CA). The current flowing through the specimen was measured with a digital multimeter (Keithley 2000, Keithley Instruments, Cleveland, OH). The voltage and current measurements were taken at 80 ms intervals.

Optical spectrometry measurements were made with AvaSpec-ULS2048 in the visible range (360–1100 nm) and on an AvaSpec-NIR256-2.5TEC for the near infrared range (1000–2500 nm). The spectrometers, from Avantes (Broomfield, CO, USA) were calibrated in wavelength and relative intensity with a standard black body radiator.

3. In situ measurements of the specimen temperature and comparison with the black body radiation model

The lattice expansion was calibrated against the specimen temperature from the shift in the diffraction peaks while the furnace temperature was increased, *without applying an electric field to the specimen*. The shifts in (1 0 1) and (1 1 1) peaks in 3YSZ, and the (1 1 1) peak from Pt were measured. The peak shifts with temperature are shown in Fig. 2(a). These data are plotted in Fig. 2(b), where the null position corresponds to 800 °C. The Pt measurements were matched to peak shifts for 3YSZ. The YSZ data were then extended to 1690 °C. The plot in Fig. 2(b) served as the calibration for estimating the specimen temperature during the flash experiments.

For the flash experiments the specimen was placed in a furnace held at 800 °C. An electric field of 120 V cm^{-1} was then applied as a step function. The flash triggered after a brief incubation time, at which point the power supply was switched to current control. The power expended in the specimen was calculated from the product of voltage and current, which was divided by the volume of the sample to express it in units of mW mm^{-3}. The typical profile for the power density is shown in Fig. 3(a). The sample was first flash sintered within the apparatus. It was then flashed again, in the dense state, for the temperature measurements. In this state the current was raised in a stepwise fashion, as shown in Fig. 3(b) in order to increase the sample temperature. The sample temperature was then obtained from the lattice expansion inserted into the calibration plot given in Fig. 2.

The power density expended in the sample was obtained from the product of the voltage measured at the specimen terminals and the current which is controlled at the power supply. In this way the power at each of the steps of the current, given in Fig. 3(b), was calculated. The power density was used to estimate the specimen temperature from the black body radiation (BBR) model [5]; this model is appropriate for the steady state

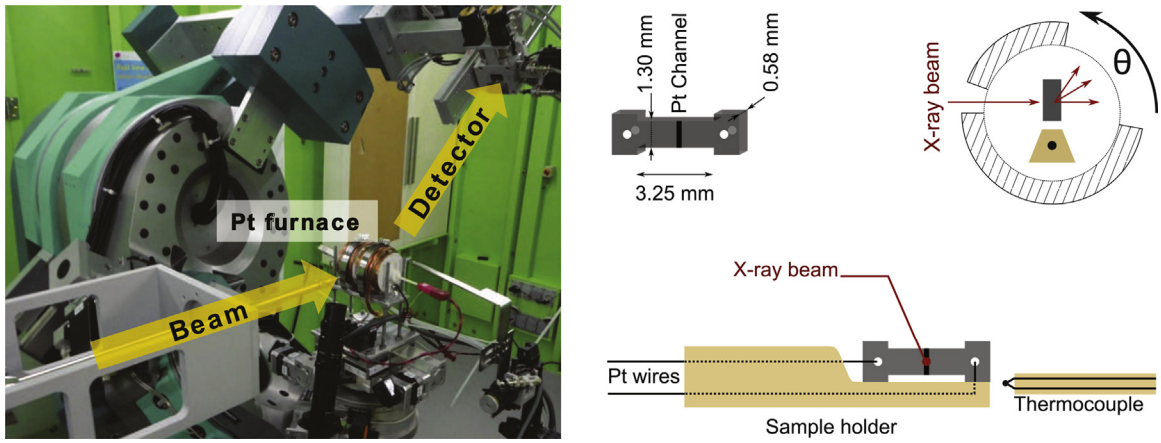

Fig. 1. The arrangement for experiments at the Pohang Light Source II. The furnace was specially designed to have as small a diameter as possible in order to ensure that the specimen temperature was the same as the temperature measured at the thermocouple. The length of the hot-zone was four times the length of the specimen. The temperature along the specimen was uniform to within ±3 °C.

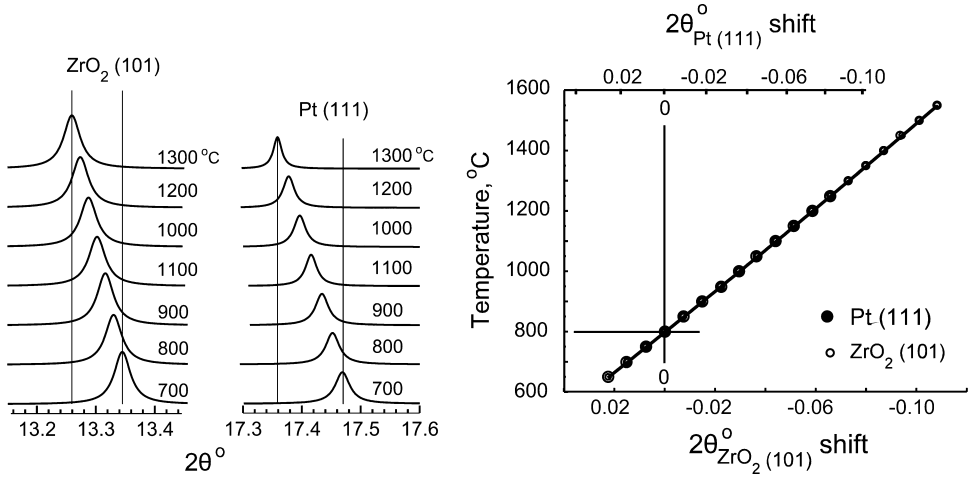

Fig. 2. The thermal expansion in zirconium oxide and in Pt is calibrated against the temperature of the furnace without the application of electrical fields. The Pt serves as a marker to check the calibration of thermal expansion in zirconia. (a) The peaks shift to lower Bragg angles as the temperature is raised. (b) Plots of the shifts in the peak positions against specimen temperature.

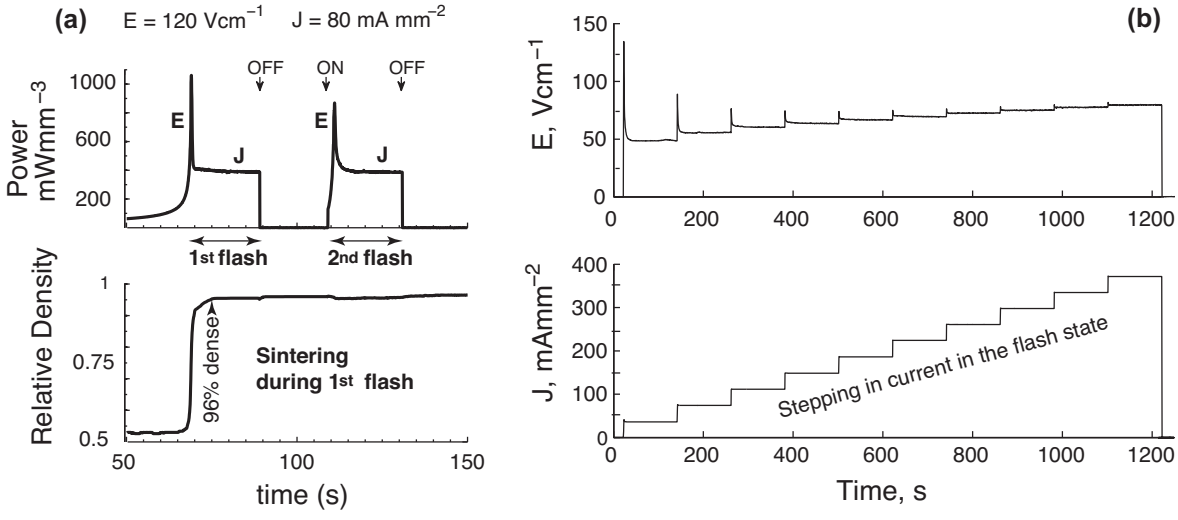

Fig. 3. The "flash" experiments were carried out at an isothermal furnace temperature of 800 °C. (a) The non-linear response of the specimen following the application of electric field; at the onset of the non-linearity at the power supply is switched from voltage to current control. (b) The current flowing through the sample is increased in steps while the sample remains in the state of flash. Higher currents lead to a higher specimen temperature.

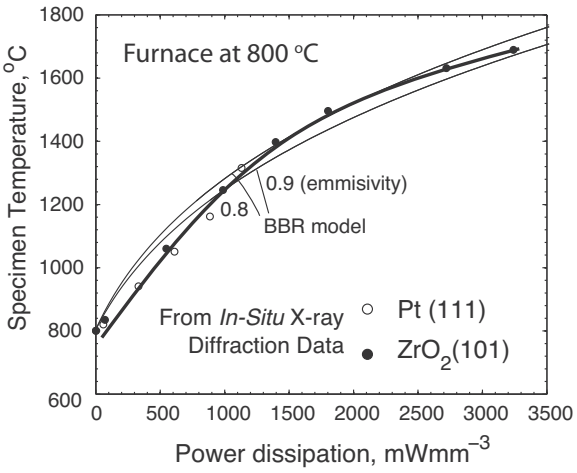

Fig. 4. Specimen temperature plotted against the power dissipation which was increased by stepping in current. The points are the temperature measurements using the calibrations in Fig. 2. The thin solid lines are the predictions from the black body radiation (BBR) model [5].

condition of the specimen since that does not involve the heat absorbed by the specific heat.

The specimen temperatures obtained from the in situ measurements of lattice expansion are compared with the predictions from the BBR model in Fig. 4, plotted for two values of the emissivity, 0.8 and 0.9. The agreement is excellent. This is a satisfying result. It shows that the BBR predictions in flash sintering experiments provide credible values for the specimen temperature, which can be helpful in understanding the fundamental mechanisms of flash sintering.

4. Spectral distribution of electroluminescence

Intense optical luminescence is a key feature of the flash phenomenon. We are now in a position to answer the question whether this luminescence is from black body radiation or from recombination of electron–hole exciton-pairs. The approach consists of measuring the optical spectrum of the emission and comparing it with what would have been expected if the emission had arisen from black body radiation. This comparison was made for several levels of specimen temperature achieved by stepwise increase in the current as given in Fig. 3(b).

The results from the spectrometer measurements are shown in Fig. 5(a). They range from 400 nm to 2.5 μm, which was obtained by stitching together data from three spectrometers; the slight discontinuities in the spectra at 1000 nm and at 1700 nm mark the transitions between them.

The above results show emission at successively higher specimen temperatures. Plots of the prediction of black body radiation at these same temperatures are given in Fig. 5(b). The spectra cover a wide range of specimen temperatures, from 990 °C to 1690 °C. The two remarkable differences between the measured spectra and the body radiation are (i) the presence of two radiation peaks from electroluminescence and (ii) the intensity of the peaks rising, but their positions remaining independent of the specimen temperature. In contrast, in black body radiation, the peak shifts toward shorter wavelengths with temperature. In the present experiments the first peak emitted from the specimen appears at 1175 nm; the specimen temperature would have to have been at 2360 °C to emit a peak at this wavelength by black body radiation, which is clearly inconsistent with the measurements of the specimen temperature.

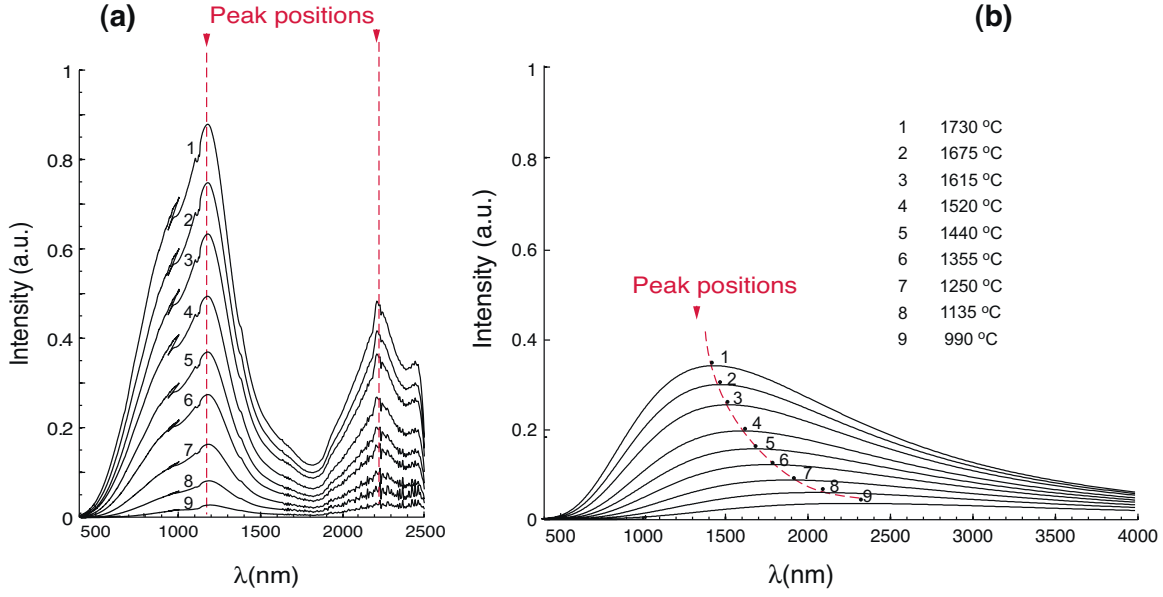

Fig. 5. (a) Electroluminescence from the specimen in the flash state. The emission intensity increases with temperature, which is a result of higher currents flowing through the specimen. Note that the position of the peaks remains unchanged while their intensity increases with temperature. (b) Theoretical black body radiation at temperatures of the specimen reported in Fig. 4; the intensity is in arbitrary units.

Fig. 6. Once the flash is instigated inside a furnace the specimen can be brought into the open and it continues to flash like a light bulb.

The stationary position for the wavelength of the emission from the specimens at different temperatures represents electroluminescence where the emission wavelength is fixed by the band gap for electron–hole recombination. The temperature increases the concentration of the electrons, which increases the intensity of emission, but the energy of the photons remains equal to the band gap.

5. Discussion

Once the specimen enters the constant state-of-flash the furnace can be removed. The specimen continues to glow. A picture of such a state, where the sample is first flashed in a furnace but then taken out into the open is shown in Fig. 6. It is immediately appreciated that the luminescing ceramic can serve a lighting device. Indeed patents issued to Nernst in 1897–1899 [6,7] in the name of a "glow-lamp", may have been the same effect. The patents were sold for one million Goldmark to the General Electric Company, and eight hundred of them lighted the World's Fair in 1900 in Paris. A description of the lamp was published in 1902 [8]. Yttria stabilized zirconia was the preferred material for constructing the Nernst Lamp, although it was recognized that many ceramics exhibited this behavior.

The electrical control for the Nernst Lamp was the same as in the flash sintering experiments. The temperature of the ceramic was raised with a secondary source until the conductivity of the glowbar increased suddenly. At this point the (DC) power supply was switched from voltage to current control, and the Lamp continued to emit in a steady state without auxiliary heating.

It is rather remarkable that now, more than a century later, we discover that in addition to luminescence the phenomenon also leads to flash sintering. It could not have been anticipated since sintering is related to mass transport, which is charge neutral, while conductivity is related to the transport of charged species. The coupling between flash sintering and electroluminescence is raising new questions about the physics underlying this phenomenon. The idea of Frenkel pairs nucleating and ionizing into charge neutral vacancies and interstitials and electron–hole pairs, however speculative, still remains the only viable mechanism [9]. However, the ionization of single charged ions, e.g. interstitials, requires fields that are much larger [10] than used in the flash experiments. A model for the ionization to take place from clusters of interstitial-vacancy dipoles by the nucleation of embryos may have value [11].

The agreement between the BBR model [5] and the in situ measurements of specimen temperature by lattice expansion, Fig. 4, is an important step toward understanding the role of Joule heating in flash sintering. However, the present results cannot be applied immediately to sintering since sintering occurs under transient conditions, when there is an abrupt increase in current and the power is switched to current control, which we have called Stage II [2]. The temperature during these transients may be higher than we measure here. This is a topic of continued research in our laboratory.

A more dynamic version of the BBR model, which includes the energy absorbed by the specific heat, has been developed for the Stage II (in process). The steady state Stage III results presented here cannot, in themselves, answer the question of whether or not flash sintering is instigated solely by Joule heating.

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